ABSTRACT

Title of Document: EVALUATING THE EFFICACY OF CATTAIL (*TYPHA SPP.*) FIBER FOR OIL SORPTION

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Oil spills pose a serious threat to aquatic life, the environment, and human health. Current methods to remove oil from waterways and mitigate damage include burning, skimming, and synthetic sorbents; however, they all have substantial limitations. Previous studies have shown that cattail (*Typha* spp.) fibers have potential as natural sorbents due to their hydrophobic and lipophilic properties. Additionally, cattail may be a more sustainable alternative than other natural sorbents including cotton. It is easily harvested, can be grown in a wide range of climates and has a smaller water footprint than cotton. The purpose of this study was to conduct a materials comparison between cattail fiber and other products such as cotton under varying water conditions for application as a sorbent during oil spill cleanup and remediation. Oil sorption of cattail and cotton was measured and expressed as gram-to-gram ratio of oil-to-fiber under a range of environmental conditions including water temperature and salinity. In cattail, the effectiveness of oil sorption decreased at higher temperatures and this also led to a decrease in selectivity in an oil/water mixture. Cotton sorbed more oil than cattail under any conditions, but also sorbed more water so cotton was not as selective as cattail in sorbing oil under moderate temperatures. These results demonstrate that cattail would be a better sorbent than cotton except in very warm waters since it is more selective

for oil compared to water, and provide information necessary for future developments in sorbent technology using cattails.

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By

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Introduction

Over 95 million barrels of oil per day were consumed globally in 2016 (IEA, 2017). The systems involving the extraction, refinement, and transportation of oil itself, however, are far from ideal. Approximately 600,000 metric tons of petroleum hydrocarbons are released into the environment every year, 53% of which are due to processes that occur before consumption (Kvenvolden & Cooper, 2003). Since oil spills can lead to serious ecological damage to sea and shore life, impact human health, and result in economic losses, ways to minimize the negative impacts of spills have been extensively researched. However, none of the current solutions are sufficient to eliminate the risk of oil spills or to prevent serious consequences when they occur. (Cheong, 2012; Day et al., 1979; Jernelöv, 2010; Kim et al., 2010; McHale et al., 2005; Suarez et al., 2011; Takawira et al., 2014).

In addition to not being very efficient under certain environmental conditions, some of these current remediation systems also have human health risks such as reduced immune system, cancer risks and developmental issues (Tamis et al., 2012). Some of these risks are associated with the use of chemicals and mechanisms that do not remove the oil from the spill site. They often just contain the oil to a small area or reduce the oil mixing and sticking to other substances (Ventikos et al., 2004). Therefore, it is important to continue to investigate the use of more sustainable and less harmful natural products for use in oil spill remediation. Recent studies have shown that cattail (*Typha* spp.) fibers have potential as natural oil sorbents due to their hydrophobic and lipophilic properties. Additionally, cattails may be present a more sustainable option than other plant species because it is nature throughout North America, grows prolifically in low-lying areas and could potentially in

low-lying areas and could potentially be harvested multiple times due to its perennial growth habit.

This study focuses on the use of a natural sorbent as a method to extract petroleum from aquatic environments. A sorbent is any material used to absorb or adsorb liquids or gases (US EPA, Terms). The study will expand the existing literature on natural sorbents by conducting a comparative study of sorption abilities of cattail fibers and cotton.

The specific purpose of this study was to evaluate the efficiency of cattails in absorbing oil under a range of environmental conditions and to compare this to materials from other plant species, such as cotton (*Gossypium* spp). For instance, temperature has been shown to affect water absorbance in the building material eastern white pine (Mukhopadhyaya et. al., 2002). Likewise, increasing concentration of salinity increased adsorption of the polymer hydrolyzed polyarylamide on sandstone rock surface (Ali & Mahmud, 2015). Increasing salinity decreases adsorbent's electric double layer—a measure of distance over which electrostatic repulsion can be felt by the adsorbate. This reduction in repulsive field between the adsorbent and the adsorbate generally leads to increased adsorption (Dimov et. al., 2002). This research aimed to demonstrate the usefulness of cattail fibers as an environmentally friendly natural sorbent to remove oil from a spill environment. This research could lead to the development of a potentially new and environmentally safe option for oil removal that does not use chemicals or synthetic products.

Research Questions

This research addresses the following questions:

1. How does the sorption of water and oil change for cattail and cotton fibers when the sorbent is in an oil/water mixture?

2. What effect does temperature have on water sorption, oil sorption, and oil selectivity for cattail and cotton fibers?
3. What effect does salinity have on water sorption, oil sorption, and oil selectivity for cattail and cotton fibers?

Hypotheses

Based on previous research, we have formed the following hypotheses:

1. Cattail fiber will be more selective to oil than cotton fiber.
2. Temperature will affect oil sorption and will not affect water sorption in cattail or cotton fibers.
3. Increased salinity levels will lead to increased oil adsorption in both cotton and cattail fibers.

Chapter I. Literature Review

Oil use and risks in transportation

Oil is used extensively and transported globally. There is a wide variation of colors and densities of petroleum due to the various possible origins and factors of its formation (Albahri, 2012). The least dense forms of petroleum are the most important to the global economy for two main reasons. Firstly, according to the United States Energy Information Administration, over 6 trillion barrels of light petroleum are consumed per year, compared to about 4.5 trillion barrels of heavy petroleum (Attanasi, 2013).. Secondly, the US uses 19.63 million barrels of oil a day (US EIA, 2017). The Eastern Hemisphere contains 85% of the world's light oil reserve, so oil needs to be transported over long distances in very high quantities, thus increasing the risk of leaks and spills into the environment.

Oil properties

Oil can vary in quality, with average crude oil containing 84% carbon, 14% hydrogen, 1 to 3% sulfur, and approximately 1% nitrogen, 1% oxygen and 0.1% minerals and salts (Twerdok, 2003). To get rid of impurities, crude oil is often brought to refineries across the world, where it is manufactured into a number of materials, including plastics, fuels, and lubricants.

One of the properties of oil that make it especially harmful to the environment is its hydrophobicity. This property stems from the fact that water molecules are polar and oil molecules are nonpolar. Water molecules will form hydrogen bonds to other water molecules, but will not bond to nonpolar substances like oil. This property means that when oil is spilled it does not break down in water as quickly as other substances do and is therefore extremely persistent in the environment (Paine, 1996). This can result in oil

blocking sunlight for aquatic photosynthesis, bioaccumulation of hydrocarbons in aquatic organisms, and the accumulation of hydrocarbons in sediment that can then be released years to decades later during disturbances of the benthic environment (Paine, 1996).

Another important property of oil is its viscosity as it affects sorption. More viscous oils have a harder time penetrating the fibers of sorbents when being collected. As oil rests on the surface of water, the lighter and more volatile components evaporate, which then increases the viscosity of the remaining oil (Teas, 2001). The longer it takes to respond to an oil spill, the more difficult it becomes to remove the oil with sorbents because of the increased viscosity of the oil layer.

Ecological, human, and economic impacts of oil spills

Inherent in the transportation of any substance is the risk of accidental spills or losses of material. In the case of oil transportation, tanker spills and pipeline blowouts, such as the Exxon Valdez and BP Deepwater Horizon accidents, receive high media coverage and mobilization of response units. However, these accidental spills account for a global average of only 10% or less of the oil entering the environment each year (Hodgson, 1990; Lee, 2014; Obama et al., 2010; Farrington, 2013). Oil slicks that damage wildlife are more commonly caused by leakage from old pipelines, processing facilities, and operational discharges like tank washing (Jernelov, 2010). The resulting loss of aquatic life and contamination of coastal, estuarine, and lacustrine sites has far-reaching effects on livelihood of the fishing industry, residents of affected areas, and tourism (Cheong, 2012).

The repercussions of oil spills, including unnatural shifts in abiotic systems like reducing moisture in the soil, are even greater when spills occur close to the shoreline (Takawira et al., 2014). The contamination of shorelines by hydrocarbons causes soils to

become hydrophobic after exposure. This process prevents the absorption of water into deep soil horizons, preventing plant roots from absorbing water and decimating plant life in the surrounding areas (McHale et al., 2005). When plants die, their root structure can no longer support the soil, ultimately leading to the erosion of beaches and shores (Jernelov, 2010). After the Hebei-Spirit oil spill in December of 2007, the Taean Region of Choognam Providence in the Republic of Korea suffered great losses in their fishing and tourism industry. The number of fish caught the following year went down by approximately 50% and the number of tourists went from almost 10 million the previous year to under 2 million (Cheong, 2012). Although these issues are only applicable when spills occur in the range of a shoreline, there are a variety of other problems that can occur in other locations.

When spills occur in open waters, the hydrocarbons mostly degrade into oil droplets. These droplets remain chemically toxic for an extended period of time. During this period, the area becomes an emulsified solution of oil and water (Kim et al., 2003). Therefore, preventing the introduction of oil droplets into deeper channels of the ocean and controlling the possible buildup of large-scale reservoirs along shorelines is imperative. When the oil droplets sink and mix with water, they can poison fish and block valuable sunlight to underwater environments. A lack of sunlight inhibits the photosynthesis of aquatic plants, which affects the entire food web and results in an excess of decaying matter because of the organisms that can no longer sustain themselves. This may culminate in selective population booms, which upset the balance of the ecosystem (Jernelov, 2010). Therefore initial responses to oil spills must be rapid and efficient.

Recovery can take decades, and until it happens, the fishing and tourism industries of shore towns experience severe economic and environmental losses (Cheong, 2012). These

negative impacts have further potential to spread to new corners of the globe, due to the migration of oiling operations. Many nations and oil companies are looking to channels off the coast and in the Arctic regions for more oil deposits and for new transportation routes, increasing the challenges of quickly and effectively responding to emergency oil spills (Kim et al., 2010).

Methods used to clean up and mitigate damage

Prevention and remediation of the negative effects of oil spills on the environment, human health, and local economies has led to the development of a suite of mitigation techniques. These can be grouped into categories of mechanical, chemical, bio-remedial and sorbent (synthetic and natural) methods. Each has its own set of advantages and disadvantages that will be discussed below (Ventikos et al., 2004).

Mechanical methods

The primary line of defense in cleaning up oil spills is mechanical, involving the containment and capture of spilled oil. These can be used in tandem with many other cleanup techniques (Ventikos et al., 2004). The most prevalent mechanical methods are booms and skimmers. Booms are physical barriers that enclose an oil spill to prevent it from spreading. While the spill is contained, an additional cleanup method is applied to the oil slick, such as skimmers (Ventikos et al., 2004). Skimmers utilize suction or adhesion to recover oil or oil-water mixtures on the surface of a body of water (Ventikos et al., 2004). However, mechanical methods are only suitable for a limited number of oil spill scenarios. These methods are heavily influenced by environmental conditions, as well as the size, nature, and location of the oil spill (United States & National Commission on the BP Deepwater Horizon Oil Spill and Offshore Drilling, 2011). For example, the Exxon Valdez oil spill occurred in a

remote location, and therefore skimmers, a relatively common mechanical device, were not immediately available. When this oil recovery method was finally available, the heavy kelp and thick oil often clogged the equipment, leading to time-consuming repairs. Meanwhile, the stormy and inclement weather slowed the cleanup operation further, creating an unwanted contingency of stagnant oil in the open water (US EPA, n.d.).

In-situ burning

Another commonly utilized oil spill cleanup method is in-situ burning, where the majority of oil hydrocarbons on the surface of a slick are combusted, breaking them down into carbon dioxide and water vapor (Ventikos et al., 2004). During the cleanup of the Deepwater Horizon oil spill, the US Coast Guard estimated that between 220,000 and 310,000 barrels of oil were burned (Schaum et al., 2010). Although this approach is a fast way to eliminate an oil slick, it generates smoke plumes that contain many of the remaining uncombusted petroleum hydrocarbons (Tamis et al., 2012). These soot emissions, which are composed of potentially hazardous polycyclic aromatic hydrocarbons (PAHs) and metals, are hazardous to human health and cannot be contained (Tamis et al., 2012; Day et al. 1979). Furthermore, this method leaves a burn residue, which is a tar-like resin containing heavier hydrocarbons that were not combusted. These heavy hydrocarbons can sink into the water column, exposing the aquatic food chain to toxins (Tamis et al., 2012). Overall, using physical methods to alleviate the effects of oil spills can prove to be inefficient and dangerous not only to the environment, but also to the human population.

Chemical methods

There are also a number of chemical methods that are utilized in oil spill cleanup efforts. These include herding agents, solidifiers, demulsifiers, and dispersants. Herding

agents, also referred to as collecting agents, are generally used to enhance the effectiveness of mechanical methods by preventing oil from sticking to objects, such as booms. The herding agents are applied to the water surface around an oil slick, compressing the oil on the perimeter of the slick. This technique makes the oil film thicker and reduces the spreading of the slick, creating a "chemical boom" which can last six to eight hours. However, this chemical barrier is much more sensitive to wave motion than a physical barrier and can only be used in placid waters. Additionally, even while the slick is contained, it may drift somewhat (Tamis et al., 2012).

Solidifying agents, such as oil congealers, are another method used to prevent the spread of a slick. This chemical method is only effective on low- to medium-viscosity oils and often increases the difficulty of separating oil from the water surface it is on. However, solidifying agents are only applicable to oil slicks on the surface of water. To solve this issue, demulsifying agents were developed for oil spill situations with oil-in-water emulsions (Tamis et al., 2012). These agents separate oil from the emulsion, allowing more oil to be collected via other methods (Ventikos et al., 2004). This also creates more environmental issues as it allows oil to seep deeper into the water column, damaging the environment below it (Tamis et al., 2012).

Chemical dispersing agents reduce the tension in the oil-water interface, causing the oil slick to split into small droplets which are dispersed in water column (Ventikos et al., 2004). Following the Deepwater Horizon oil spill, approximately 1.84 million gallons of dispersants were applied to the surface of the ocean directly on the oil slick and released next to the source of the spill (United States & National Commission on the BP Deepwater Horizon Oil Spill and Offshore Drilling, 2011). Increasing the dispersion rate of an oil slick

can prevent harm to sea birds and mammals and stop the slick from reaching coastlines (Tamis et al., 2012).

Although dispersants eliminate oil from the surface of the water, this chemical method causes the water column to be contaminated with oil, which adversely affects aquatic life. This method cannot be applied to thin layers of oil and cannot properly disperse dense or weathered oils. Dispersants are also unable to affect oil-water emulsions (Tamis et al., 2012). While dispersants are largely successful at protecting birds and beaches, they have been shown to be unreliable in certain environmental conditions (Fuller et al., 2004; US EPA). For example, during the cleanup of the Exxon Valdez oil spill, dispersants were among the first solutions implemented by the Coast Guard; however, it was quickly determined that the dispersants were ineffective due to insufficient wave motion (US EPA). Additional studies have shown that factors such as mixing energy (i.e. wave motion), oil weathering, oil viscosity, and water temperature have a large impact on the effectiveness of dispersants (Mukherjee & Wrenn, 2011; Chandrasekar et al., 2005). In addition, the usage of dispersants is still controversial because the toxicity of dispersants and their impact on both human and environmental health are not yet fully understood. A study conducted by researchers at Texas A&M University found the toxicity of the dispersant itself to be negligible in comparison to the toxicity of oil (Fuller et al., 2004). However, a more recent study found that the oil droplets that are dispersed into the water column retain their toxicity, resulting in increased damage to subsurface ecosystems (Jernelöv, 2010). In addition, a retrospective study conducted after the Deepwater Horizon oil spill found that cleanup workers who were exposed to dispersants experienced marked changes in blood chemistry, liver enzymes, and experienced physical symptoms and discomfort (D'Andrea & Reddy,

2013). Despite the uncertainty of toxicity, the EPA has approved over 40 chemical dispersants to cleanup oil spills (US EPA, 2014). Thus, despite toxicity and effectiveness concerns, dispersants are still a widely used solution.

Bioremediation Methods

While dispersants aim to dilute the toxicity of an oil slick by dispersing it within the water column, bioremediation techniques decrease toxicity by breaking down the petroleum hydrocarbons into less harmful compounds (Ventikos et al., 2004). This method is suitable for oil recovery in areas where large mechanical methods would hurt surrounding plant and wildlife, such as salt marshes or shorelines. Oil-eating bacteria, often applied in cyanobacterial mats, have proven to be effective in speeding up the natural degradation process of the oil spills on coasts (Tamis et al., 2012). In addition, the method of using cyanobacteria comes with the unique advantage of natural selection. Researchers have found that exposing sulfate-reducing bacteria to oil droplets enhances oil degradation in future generations to degrade oil faster (Lu et al., 2012). However, the method has serious downsides. Eventual die-offs of cyanobacteria when placed in excess oil can lead to eutrophication from the release of excess nutrients into the water and low oxygen content of the water. This leads to dead zones that decimate benthic organisms and severely disrupt the aquatic ecosystem as a whole. Therefore, bioremediation of the form cannot be applied in deep waters, where oxygen is limited (Tamis et al., 2012).

Sorbents

Oil spills can also be remedied by using natural and synthetic sorbents to clean up the entire spill or remaining areas that were not initially cleaned. Sorbents are a widely used

method due to their low cost and their ability to remove high amounts of oil (Wahi et al., 2013). Sorbents can be divided into two classes – absorbents and adsorbents (ITOPF, 2012).

Sorption mechanisms

Absorbents are materials through which liquid permeates while adsorbents are materials that attract liquid to their surfaces (Weisman, 1986). Absorption takes an extended period of time to be completed, and it is extremely difficult to recover absorbed oil from a sorbent that exhibits this mechanism. Most of the sorbents used in oil spills are therefore adsorbents. Being oleophilic and hydrophobic are the two main factors that enhance the efficiency of a sorbent (Sun et al., 2002). Being non-polar, which makes it difficult for a substance to bond with water, allows the substance to attract nonpolar oil much better. Other properties that define an efficient and effective sorbent are surface area, buoyancy, and reusability (Teas et al., 2001; ITOPF, 2012). A sorbent with a higher surface area will have more available locations for the oil to be sorbed. Having high buoyancy enables the sorbent to remain on the surface of the water, as opposed to beneath the oil slick. The buoyancy of a sorbent is more dependent on the hydrophobicity of the material rather than its density, allowing heavier sorbents to still prove effective (Korhonen et al., 2011). Conversely, lightweight sorbents are generally less effective, because if a sorbent is too buoyant, the heavier, more viscous oils will not be sorbed. Reusability does not have a direct effect on the amount of oil initially adsorbed, but is important for waste disposal. A sorbent will be considered more efficient if it is able to remove more oil throughout its entire life cycle (ITOPF, 2012).

Types of physical forms

Sorbents can be divided into four physical forms: bulk, enclosed, continuous, and loose fiber (ITOPF, 2012). Bulk sorbents are loose materials, which have little to no applicability in oceans because of the difficulty involved in recapturing the materials. In addition, the loose fibers can block nearby pipelines or, when used in tandem with mechanical methods, jam gears (Fingas, 2012). However, bulk sorbents provide a large amount of surface area where the oil can be sorbed, which makes them highly effective (Merlin & Le Guerroue, 2009). Enclosed sorbents are bulk materials enclosed in some other material such as mesh or fabric, creating pillows or booms that can be directly put on site of an oil spill (Fingas, 2012). Continuous sorbents are currently the most popular method used to clean up oil spills. These sorbents are thin and of a more constant thickness, like a pad or a mat (ITOPF, 2012). Lastly, loose fiber sorbents are the most effective method to capture weathered oils. These sorbents are made of synthetic materials, primarily polypropylene (ITOPF, 2012; Merlin & Le Guerroue, 2009). Loose fiber sorbents, unlike bulk loose sorbents, are typically in the shape of pom-poms or mop heads. The loose threads of the sorbent material are bound together but allowed to spread out, increasing the sorbent's overall surface area (Merlin & Le Guerroue, 2009; Fingas, 2012).

Types of sorbents

Most sorbents can be grouped into three different categories: inorganic minerals, synthetic sorbents, and organic vegetables (or natural sorbents) (Teas et al., 2001; ITOPF, 2012).

Inorganic minerals

Inorganic minerals are minerals that cannot be easily digested by organisms and are readily available in nature. Examples include compounds such as perlite, clay, vermiculite,

and sand (Teas et al., 2001). Inorganic minerals are restricted in application because they cannot be used at the site of a spill and generally have low buoyancy and sorption (Choi & Cloud, 1992). Therefore, they are primarily used as a filter for wastewater or water that may have been contaminated with oils (ITOPF, 2012).

Synthetic sorbents

Synthetic sorbents are man-made materials designed to adsorb liquids onto their surfaces. Examples include polypropylene and foam (Sun et al., 2002). Synthetic sorbents are the most prevalent, since they generally have high affinity to oil and high sorption rates. However, they usually have slow degradation rates, which allows waste material to accumulate, and are not as available as inorganic minerals or organic vegetables (ITOPF, 2012).

Organic vegetables

Organic vegetables include crops such as cotton and rice hulls (Singh et al., 2013). Although organic vegetables have high degradation rates and are readily available, they are typically the hardest sorbent type to work with since they have relatively low buoyancy, sorption, and hydrophobicity (Teas et al., 2001; Adebajo et al., 2003). Rice hull, an organic vegetable, is the quintessential example of a natural sorbent. Tested as a sorbent of different types of oil, researchers found that it picked up 88% of engine oil, 80% of spent oil (waste oil), and 55% of unrefined oil. However, the sorption rates decreased after five minutes of exposure to the oil (Razavi, 2014).

Research has been done on limiting the drawbacks and enhancing the properties of sorbents. Certain sorbents can be chemically altered in order to increase their effectiveness. For example, spraying titanium dioxide on aerogels, synthetic material with a large gas

component, increases their hydrophobicity as well as their buoyancy (Korhonen et al., 2011). Another example of chemical alteration is performing acetylation (i.e. adding an acetyl group to the compound) to rice hulls to increase the hulls' capacity to sorb oil (Sun et al., 2002). It is also possible to create hybrid sorbents using natural and synthetic materials to maximize sorption and biodegradability (Choi & Cloud, 1992).

Out of the many current solutions to oil spills, natural sorbents have the highest potential to clean up oil spills sustainably, since natural sorbents need little equipment to produce (unlike synthetic sorbents) and are biodegradable (Choi, 1992). However, current natural sorbents are not as effective at sorbing oil and have lower hydrophobicity compared to synthetic sorbents. Nevertheless, natural sorbents' biodegradability and abundance is highly sustainable and cost effective, which calls for more research on natural sorbents aiming to get better selective adsorption of oil.

Kapok

Due to its surface wax content of 3%, kapok fiber is hydrophobic and therefore will naturally attract the non-polar hydrocarbons in crude oil, causing them to bond to the surface of the fiber. This wax content is much lower than the 10.64% wax content of cattail fiber, though higher than other natural sorbents, such as cotton (Dong et al., 2015b). Because most of the oil is collected via absorption into the fiber, this oil can easily be recovered via centrifugation. Once the oil is centrifuged out of the sorbent, it can be degraded and harnessed for biomass energy, making it a sustainable process. This would not be possible with a synthetic sorbent, because those fibers would not degrade (Lim & Huang, 2007).

Cotton

Cotton fiber is less hydrophobic than kapok fiber, with a wax content ranging from 0.6-0.8%, which greatly diminishes its selectivity of oil to water (Dong et al., 2015b). This fiber sorbs oil using the processes of adsorption, absorption, and interfiber capillary action (Singh et al., 2013). Each fiber of cotton is quite fine, causing the sorbent to have a large surface area overall on which to collect oil (Singh et al., 2013).

Sorbent Hybrids

Blended sorbent fiber assemblies harness the strengths of each sorbent utilized. For example, cattail-kapok hybrids have high oil sorption capabilities due to kapok fibers while maintaining high selectivity due to cattail fibers (Dong et al., 2015b). In addition, mixing natural sorbents with some synthetic fibers can increase their selectivity and sorption abilities, though it ultimately causes the product to not be completely biodegradable (Dong et al., 2015b).

Cattail fibers

Cattail fiber is found in the cattail plant, a wetland plant species found mostly in the Northern Hemisphere (Mitich, 2009). The fibers are attached to the small seeds located in the female flower, or seedhead, of the plant (see Appendix A). When the dense female pistil is opened, the fibers and seeds are released, in order to enhance seed dispersal by wind (see Appendix A). These plants also have a rapid growth rate, making them a plentiful resource for a character study of their fiber (Mitich, 2009). The fibers themselves have important material properties that make them a viable option for use as a natural sorbent (Cui et al., 2012; Grace & Wetzel, 1982; Khan et al., 2004; Pankratz et al., 2007; Wahi et al., 2013). Previous studies have shown cattail fibers have the potential to be efficient sorbents but more research is needed (Cao et al., 2016). The main research goal of this investigation is to

evaluate the effectiveness and viability of these fibers for use as a natural sorbent in the removal of total petroleum hydrocarbons (TPH) from aquatic environments.

Two cattail species native to North America are viable candidates for use as an organic vegetable natural sorbent. *Typha latifolia L*, the common cattail, is referred to as the broad leaf cattail, and *Typha angustifolia L,* the southern cattail, is also known as the narrow leaf cattail. Both species of cattail can be found throughout North America in wetlands, such as the shores of lakes and oceans (Mitich, 2009). These resilient plants can flourish in both dry and humid climate conditions, as long as they grow in shallow aquatic environments, and tolerate below-freezing temperatures. Common cattail reproduces through rhizome growth, but can also germinate from seeds at shorelines. Because of its high reproduction rate, it is often referred to as a weed (Mitch, 2009). A cattail-based product could be manufactured economically, since cattails are one of the most commonly found plants in marshes and shallow waters throughout the world (Kim et al., 2003).

Cattail (*Typha* spp) have many properties that make them an ideal natural sorbent to clean up oil spills (Cui et al., 2012; Grace & Wetzel, 1982; Khan et al., 2004; Wahi et al., 2013). The ability of cattail fiber to adsorb oil is due to its highly oleophilic and hydrophobic properties as well as its high surface area (Khan et al., 2004; Wahi et al., 2013; Dong et al., 2015b). Large surface area of cattail fiber is due to its highly porous morphology (Grace & Wetzel, 1982). These pores are responsible for not only sorption of oil, but also its retention (Dong et al., 2015b). Furthermore, cattail fiber has high oil-to-water selectivity due to low surface energy, high ratio of dispersion to polar components, and high wax content of 10.64% (Dong et al., 2015b). In comparison, cotton's wax content is 0.6-0.8%, compared to

3% for kapok fibers. When applied to a spill site, cattail fiber will strongly attract and adsorb the oil to its surface without accumulating water to its surface (Cui et al., 2012).

The primary variable being examined is adsorption, which is a sorbent's ability to attract molecules of another substance to its surface (US EPA, n.d.). For example, in this investigation, when cattail fiber is dropped in an oil-water mixture, the oil particles sticking to the surface of the plant fiber and creating a thin film around the fiber is considered adsorption (US EPA, n.d.). Absorbency is related to the polarity of both the sorbent and the material it is adsorbing, the sorbate. A polar sorbent will more easily adsorb a polar sorbate, as it has similar molecular characteristics to the sorbate (Loudon, 2009, pp. 340-342). Similarly, a non-polar sorbent will more easily adsorb a non-polar sorbate for the same reason. The use of cattails is justified in that both the surface of the cattail fiber and oil are nonpolar, unlike water, meaning that oil has limited solubility in water but is readily attracted to cattail fiber (Wahi et al., 2013). Therefore, cattail fibers are considered oleophilic and hydrophobic, hence forming the fundamental properties that give this material a strong potential for being used as a sorbent in the case of an oil spill (Khan et al., 2004). Existing literature has demonstrated that cattail fiber performed well in comparative studies with other sorbents for its adsorption of non-polar compounds (Khan et al., 2007; Ren et al., 2011; Teas et al., 2001). These studies have shown that in addition to being more effective, in terms of amount adsorbed per gram of cattail fiber, cattail fiber is also an organic vegetable sorbent, and completely biodegradable. These additional characteristics suggest that, once the material is manipulated into an effective form, it could be considered a more sustainable and environmentally friendly alternative to existing methods used to clean spill environments. To

bolster this claim, we investigated cattail fibers' adsorption ability in different environmental conditions.

Disposal of sorbents

The main concern with using sorbents for oil spills is the disposal of the material afterwards. Disposal of oiled sorbents are locally and federally regulated due to environmental hazards. Sorbents can be reused, degraded, incinerated, or disposed in landfills as means of removal (Fingas, 2012; ITOPF, 2012). Some are reusable after rinsing non-polar solvents through the material or compressing the material until the adsorbed oil is released (Korhonen et al., 2011; Choi & Cloud, 1992; ITOPF, 2012). The problems with continuous reuse of sorbents are increased contamination and decreased durability (ITOPF, 2012). Other sorbents are biodegradable, including all organic vegetable sorbents. If the sorbents are not biodegradable or worn down, they may be incinerated. Only sorbents that are combustible and not waterlogged can be incinerated. (ITOPF, 2012). Incineration is more expensive and regulated due to the toxins released during burning. However, this disposal option will reduce the amount of materials left in landfills (Merlin & Le Guerroue, 2009; ITOPF, 2012). The final disposal method is using landfills. This method can easily produce hazardous runoff to the ground and even place the toxic material back into the water (ITOPF, 2012).

Rationale for current research

A review of commonly used oil spill clean-up techniques shows that these current cleanup methods are either ineffective or even harmful to the environment (Aguilera, Méndez, Pásaro, & Laffon, 2010; Smith, & Ashcroft, 2011).

With an increased risk for oil spills and the potential of cattail fibers as a natural sorbent, a cattail-based product would be revolutionary to oil spill response techniques. In a comparative study of cattail fiber, kapok fiber, and a standard polyester fiber, the adsorption and retention of seven different PAHs commonly found in urban runoffs were tested and compared with each other (Khan et al., 2007). The PAHs tested were naphthalene, anthracene, acenaphthylene, acenaphthene, phenanthrene, fluoranthene, and fluorene, all nonpolar substances similar to petroleum hydrocarbons. Kapok fiber exhibited the worst sorption and desorption (a process in which molecules stick on the surface of the sorbent and are released) capacity out of the three sorbents. Cattail proved to have much better sorbent and retention rates than polyester fiber on naphthalene. Both cattail and polyester fiber performed approximately equally for all the other PAHs tested. It was also found that about 1 gram of cattails could remove 0.1 to 11 milligrams of PAHs. Even in competitive conditions, when two PAHs were present in the solution at once, cattail fiber had the highest sorption of the mixture (Khan et al., 2007).

Recognizing such adsorption abilities of cattail fibers, attempts have been made in preparing cattail fiber-based activated carbon (CFAC) and testing the product's sorption capacity in various solutions (Ren et al., 2011; Shi et al., 2010). Activated carbon is the product of pyrolysis, or subjecting an organic material high in carbon content to very high temperatures and subsequent physical or chemical treatment. The end product is highly porous with large surface area and increased adsorption capacity. Although cattail stems have been used in the past to prepare activated carbon, cattail fiber itself had rarely been used as an activated carbon source prior to 2011, when a study by Ren et al. (2011) demonstrated CFAC's adsorption ability to sorb 2,4-dichlorophenol (2,4-DCP) and 2,4,6-trichlorophenol

(2,4,6-TCP). 2,4-DCP and 2,4,6-TCP are aromatic compounds, resembling the structure of some aromatic petroleum compounds. CFAC created using a chemical activation method was found to have a relatively large Brunauer-Emmett-Teller (BET) surface area of 890.27 m^2/g. BET surface area accounts for both external surface area and pore area. Adsorption is directly proportional to BET surface. Because of its large surface area, CFAC proved to be an excellent adsorbent when applied to 2,4-DCP and 2,4,6-TCP, with a maximum adsorption rate of 124.3 milligrams of solution per gram of cattail (mg/g) and 172.4 mg/g, respectively. These were the best reaction results of all the tested conditions. The results show that cattail fibers are an extremely potent source of activated carbon. This research suggests that cattails can be effective in removing aromatic petroleum compounds, which justifies the selection of cattail fibers for use in oil spill cleanup (Ren et al., 2011).

A similar study sought to maximize adsorption capacity of CFAC by varying reaction conditions during the treatment of cattail fibers with phosphoric acid (Shi et al., 2010). Impregnation time (i.e. treatment time), activated temperature (i.e. the temperature of the cattail when soaked with phosphoric acid), and activated time (i.e. the amount of time the wet mass was heated) were found to affect BET surface area. In order from most to least effect on BET surface area are: activated temperature, activated time, impregnation ratio, and impregnation time. When all of the optimum conditions for the variables were used to prepare CFAC, the highest BET surface area of this experiment observed was 1279 m^2/g. It is important to note that this BET surface area is larger than the 890.27 m^2/g determined by Ren et al. (2011). This shows that with experimentation in various reaction conditions, the BET surface area of the output can be increased, leading to a product with better adsorption capacity. BET surface area is only one of the characteristics out of other possible variables,

which may affect adsorption ability of CFAC. This demands various experimentations with cattails in an effort to bolster its already good adsorption ability (Shi et al., 2010).

Another advantage of using a cattail fiber-based product for low remediation materials is the low cost of the raw material. Cattails are one of the most commonly found plants in marshes and shallow waters throughout the world (Kim et al., 2003), and this would be abundant as a source for materials. Furthermore the seeds could be harvested without killing the plants since cattails are perennials. This would enhance the sustainability of the product as the functional role of cattail in wetland ecology would remain largely intact.

Literature Summary

In summary, numerous research studies outlining various methods to clean up oil spills do currently exist. Furthermore, many studies have compared and contrasted, tested and refined many of the current methods out there, yet these methods still have major drawbacks. Chemical dispersants have been shown to ultimately be toxic to subsurface ecosystems (Jernelöv, 2010). Mechanical methods have several limitations, including posing danger to the ecosystem and humans as well as being costly to produce and distribute, thus limiting the use of these methods due to its dangers to air quality, human life, and inabilities to perform in a range of different environmental conditions (Schaum et al., 2010; United States & National Commission on the BP Deepwater Horizon Oil Spill and Offshore Drilling, 2011). Synthetic and natural sorbents seem the most promising to date, but they too are not without their shortcomings. Often, these sorbents are able to collect the oil without a problem, but when used continuously, these sorbents can become polluted and lose their sturdiness (ITOPF, 2012). Rice hull, a natural sorbent, is a perfect example of this weakness, since it is unable to maintain more than five minutes of contact with oil (Razavi et al., 2014).

With the multiple different sorbents available on the market, it can be challenging to determine the best one for the task of cleaning up oil spills. This is where a cattail fiber-based product has the potential to compete. The cattail plant has known properties, such as its ability to sorb heavy metals as well as it's highly oleophilic nature, that promote its untapped potential as a natural sorbent for oil spill cleanup (Pankratz et al., 2007). The culmination of limitations of current methods, in conjunction with the potential of cattail fibers as a solution, establishes the opportunity to evaluate cattail fiber-based product that could lead to the development of a novel, sustainable, effective, and economically viable option to combat major and minor oil spills. Therefore, the purpose of this study is to conduct research that addresses this need.

Chapter II. Phase 1: Proof of Concept

Introduction

In phase 1 of our experiment we conducted a series of proof of concept experiments and also focused on developing and refining our methods to limit error and standardize our procedures for phase 2. Our proof of concept experiments focused on assessing the sorption of oil by cattail fiber in standard conditions and comparing this to other natural sorbents,

namely, cotton and rice hulls. Previous research suggests that cattail fibers may be as effective or superior to other natural materials at sorbing oil due to its lipophilic and hydrophobic properties. In this phase we assessed this in our own laboratory trials and established standard methods for the rest of our study.

In Phase 1 we ran experiments designed to better understand the three basic properties of saturation time, retention time, and selectivity for oil or water sorption in natural sorbents including cattail, cotton, and rice hulls. In order to make these measurements, we had to develop experimental protocols to test these parameters. These included procedures to separate non-sorbed oil from sorbed oil (e.g. drip time) and methods to quantify water sorption vs. oil sorption, which will be referred to as "selectivity." Details on method development can be found in Appendix B.

By the end of Phase 1, we developed a method for containing the cotton and cattail fibers while they were soaking in oil and water. This was accomplished by making packets out of tulle, which we continued to use in Phase 2. Phase 1 consisted of three sets of experiments: testing saturation, retention and selectivity of the sorbents. Saturation refers to how long it takes for the fibers to pick up, or sorb, the oil while retention refers to the duration of time fibers will hold oil before it drips out. Our expectations were that maximum sorption would occur rapidly and that excess oil could be allowed to drip off within about 15 minutes. This is consistent with the existing literature (Dong et al., 2015b). We used the saturation and retention data to calculate optimum soaking and dripping times for subsequent experiments. Finally, we ran selectivity tests to find the ratio of oil to water sorbed when the fibers were exposed to a homogenous mixture of the two.

Materials and Methods

Fiber preparation

We collected cattail (*Typha latifolia L*) fibers from the banks of Campus creek at the University of Maryland in College Park, MD. *T. latifolia* readily hybridizes with *T. angustifiolia L.* so even though *T. latifolia* is the much more common and native cattail species, we could not rule out the possibility that our collection was a hybrid of the two species (Stevens & Hoag, 2006). Therefore we refer to our fibers as *Typha* spp or simply "cattail" to refer to the genus. In addition, we purchased cotton fibers from Organic Cotton Plus (SKU#13000RAW) and Rice Hulls from Home Brew Ohio (model number 45-PA0A-CP0T).

Following collection, the seed heads were broken apart in order to release the individual seed fibers. Following this, these cattail fibers as well as the cotton fibers and rice hulls were kept in a VWR drying oven (model number 1690, VWR, Radnor, PA) at 60°C for a minimum of three days in order to remove naturally-occurring moisture that could affect the sorption of oil and/or water. Between trials, fibers were kept in an oven at 50°C to prevent the re-sorption of moisture from the air. Trials were performed by submerging fibers into 600 mL beakers filled with 150mL of either oil, water, or a 200 mL mixture of both (150 mL oil and 50 mL water).

In order to keep the fibers together, we tried several methods (Appendix B) and eventually developed a procedure to make 0.50-gram tulle packets to contain the fibers. The original procedure of pouring the oil and loose fibers over tulle which we used during our saturation test was too inconsistent for the novel experiments, because the tulle was not laid completely flat over the beakers and allowed oil to collect in the middle, leading to an

overestimation of the amount of oil sorbed by the fibers. Each packet was made from tulle, heat sealed by an impulse sealer (ULINE brand), and stuffed with 0.50 grams of either cotton or cattail fiber. The packets were also kept in the drying oven between trials. In order to control as much as possible for surface area, we used a 3.5" by 6" piece of tulle folded in half and sealed on the remaining three sides for each packet.

Saturation

To understand the sorption rate of each natural sorbent, a saturation study was conducted. We placed 1.0g of loose cattail fibers in beakers containing 150 mL of SAE 10W-30 motor oil (Castrol Limited, Swindon, England) and let them soak for one of six different time intervals – 5, 10, 15, 30, 45, and 60 minutes. After the allotted amount of time, the oil and fibers were poured over a tulle filter (Figure 2.1) and left to drip into a beaker for 15 minutes, allowing excess oil not sorbed by the fiber to continue being filtered through the tulle. The tulle was secured so that the fibers could drip over the beaker while remaining flat. After the 15 minute drip time the fibers were transferred to a weigh boat and the mass was determined with a balance (Denver Instrument Company, Serial No. N0093858). Mass sorbed was determined by subtracting the initial fiber mass from the final mass. We conducted at least four trials for each material (cattail fiber, cotton fiber, and rice hull) at each of the six time intervals for a total of at least 48 trials for each material studied.

Retention

Next we determined what we termed "retention" of the fibers. This was in effect the time required to remove, by dripping, superfluous oil or water not sorbed on or into the fibers during sorption. In order to model this drip time, or retention, of oil or water by the cattail and cotton fibers, we placed 1.0 gram of fiber in 150mL of oil for 5 minutes. This time

interval was determined by the saturation study described above. After 5 minutes the fibers were then poured over a tulle filter, again using the same setup from the saturation study (Figure 2.1). We allowed the fibers to drip for one of 8 different time intervals; 5, 10, 15, 30, 45, 60, and 120 minutes. We also conducted 3-, 6-, 24-, and 48-hour trials. At the end of the specified time, the fibers were transferred to a weigh boat and massed. Eight samples of each material, cattail and cotton, were measured for each period of time.

Figure 2.1. Cattail fibers being poured over tulle and left to drip. This system was used in both saturation and retention trials during Phase 1.

Selectivity

Finally, we determined the relative sorption of oil or water and whether sorption characteristics varied in oil, water, and oil-water mixes. This we termed "selectivity" of the fibers tested. In order to understand the selectivity properties of each natural sorbent we created an emulsified oil-water mixture and conducted a set of selectivity trials. To do this

we collected data with both natural sorbents, cattail and cotton fibers, in oil, water, and an oil-water mixture. We tested four trials for each type of natural sorbent.

The oil-water mix was emulsified using a Lab-Line Orbital Shaker Model #3520 (manufactured by Lab-Line Instruments, Inc.) and we found that in order to attain complete homogenization, we needed to mix 50mL of water and 150mL of oil in a 600mL beaker for 2 minutes at 280 rpm. This ensured that the mixture stayed homogenized for over 5 minutes, the duration of time that each packet was immersed in the mixture. For each trial a packet of natural sorbent prepared as described above was weighed and placed in a beaker of the oil-water mix for 5 minutes, enabling it to saturate to its full capacity of liquid. After this time, the packet was placed on a drying rack (Figure 2.2) for 15 minutes, allowing excess liquid to drain off the packet according to the procedures developed above for saturation and retention. After this, the packet was weighed again and then placed in a drying oven and heated to at least 50°C until mass loss was less than 0.01g per day. At this point the water was presumed to have been evaporated and packets were reweighed. Total absorption of oil and water was defined as the initial mass after 15 minutes of drip time. Water absorption was determined as the mass loss over the drying time and oil sorption was defined as the initial mass after dripping minus the final mass after water had been evaporated. To ensure these methods allowed for only water evaporation, with no changes to oil content, packets of oil with no water were also placed in the oven and weighed periodically to verify that oil mass remained constant.

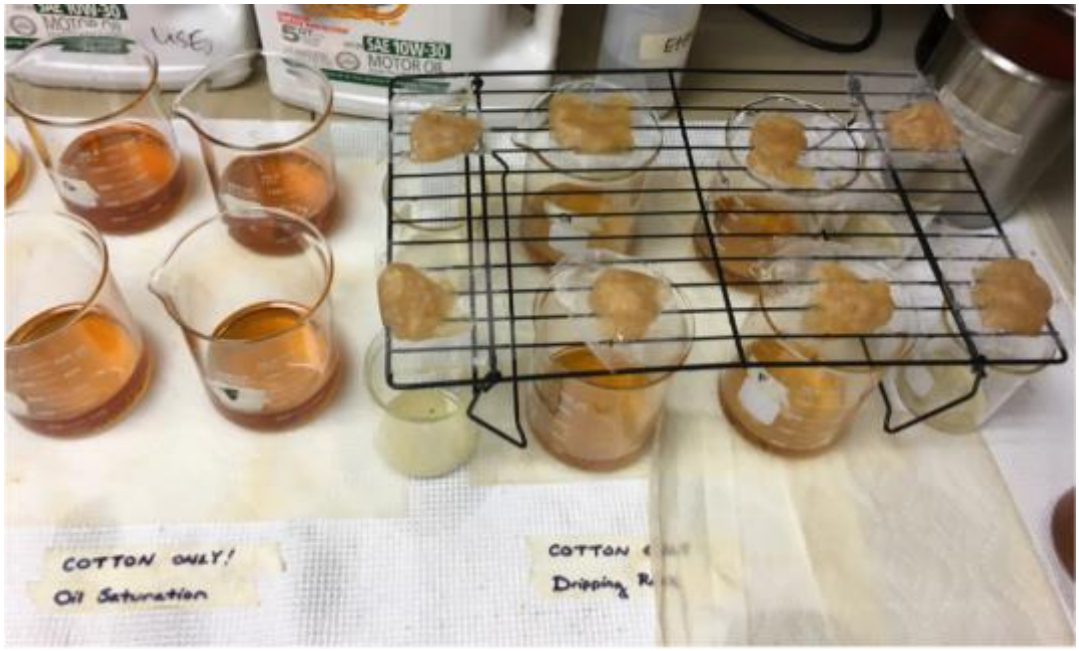

Figure 2.2. Beakers on the left used for saturating the packets in either oil, water, or an oil water mix for 5 minutes. On the right is a drying rack where packets were transferred to and allowed to drip for 15 minutes. Beakers beneath each packet were used to catch the excess liquid that was not sorbed by the fibers.

Statistical analysis

The experiment used a randomized sampling design with at least 4 samples for each measurement. Data were analysed with a one-way ANOVA for each species (cattail, cotton, and rice hulls) with sorption time as the main effect. Mean separation was completed with the Tukey multiple mean separation method. Both analysis methods used a confidence interval of 95%.

Results

Saturation

Time of exposure to oil had no significant effect on cattail fibers or rice hulls, ($P < 0.844$ and $P < 0.463$, respectively) in the amount of oil sorbed across 5-60 minutes of oil exposure. Cotton, however, showed a difference ($P<0.043$) in oil sorbed between 5 and 60 minutes. A paired t-test confirmed that oil sorption at 5 minute differed from that at 60 minutes ($P < 0.028$). A suspected outlier was removed with Dixon's Q test with 90% confidence. Further analysis yielded no significant level of variance ($P < 0.083$). Therefore it was determined that a soaking time of 5 minutes was sufficient for further studies.

Overall, both cattail and cotton sorbed substantial amounts of oil. The average amount of oil retained after treating time as a constant was 26.39 ± 2.82 g/g for cattail fibers, 37.74 ± 3.34 g/g for cotton fibers, and 4.54 ± 0.72 g/g for rice hulls (Figure 2.3). Because of their low capacity to sorb oil, rice hulls were dropped from any further use in this study.

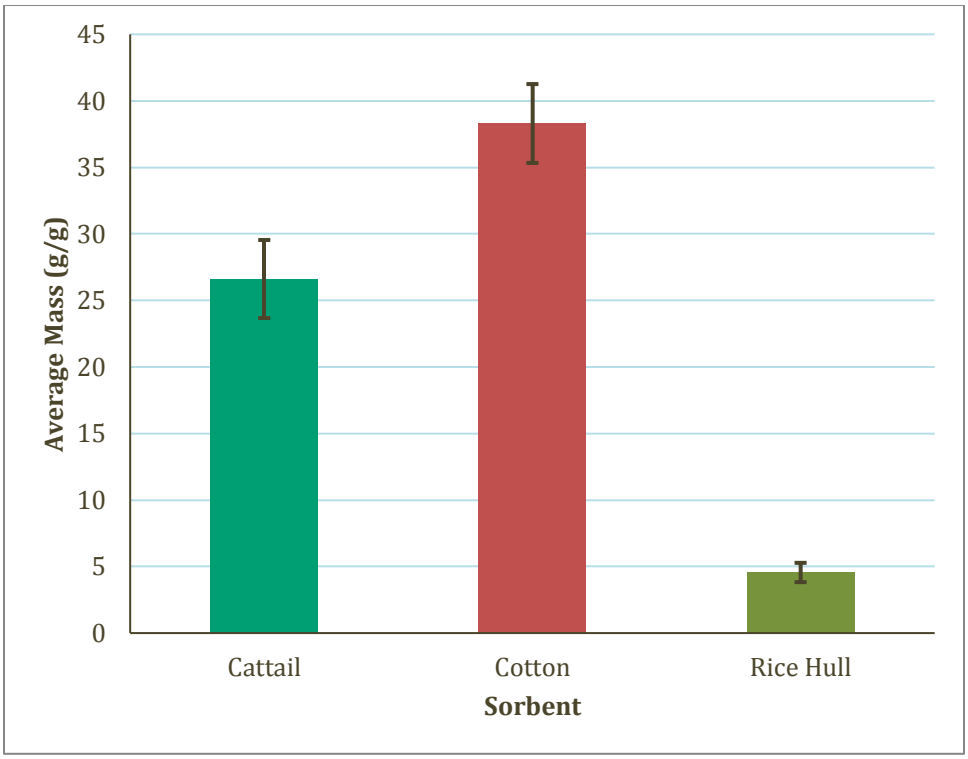

Figure 2.3. Mass of oil sorbed in 0.50 g packets of cattail, cotton or rice hull fibers soaked in motor oil (10W-30) for 5 minutes and then weighed after 15 minutes. Each bar is the mean of each material's respective total trials (Cattail = 24, Cotton = 30, Rice Hull = 30). Error bars are ± 1 SD**.**

Drip time

Mass of oil sorbed by both cattail or cotton decreased rapidly over the first 10 to 15 minutes and then remained relatively stable for up to 48 hours (data only shown to 120 minutes in cattail and 60 minutes in cotton) (Figure 2.4). As in the previous test, sorption was much greater in cotton compared to cattail fiber.

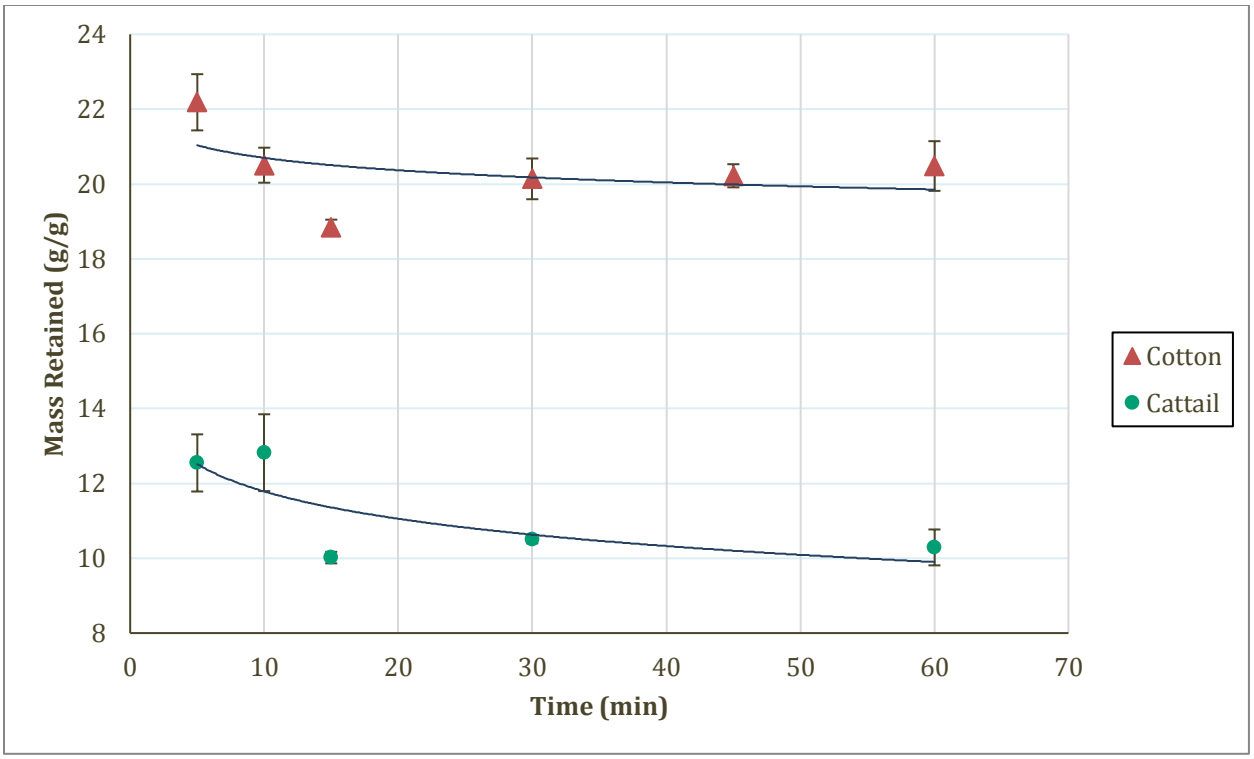

Figure 2.4. Mass of oil sorbed in 0.50 g packets of cattail or cotton fibers soaked in motor oil (10W-30) for 5 minutes and then weighed after a dripping time of 4 to 120 minutes. Each point is the mean of 8 trials. Error bars are ± 1 SE.

Selectivity

Cotton fiber had greater oil and water sorption compared to cattail fiber. However, the increase in cotton's sorption compared to cattail was not proportional (Figure 2.5). The ratio of oil to water sorption was 5.6:1 for cattail and 4.0:1 for cotton when calculated in sorption trials in an oil-water emulsion.

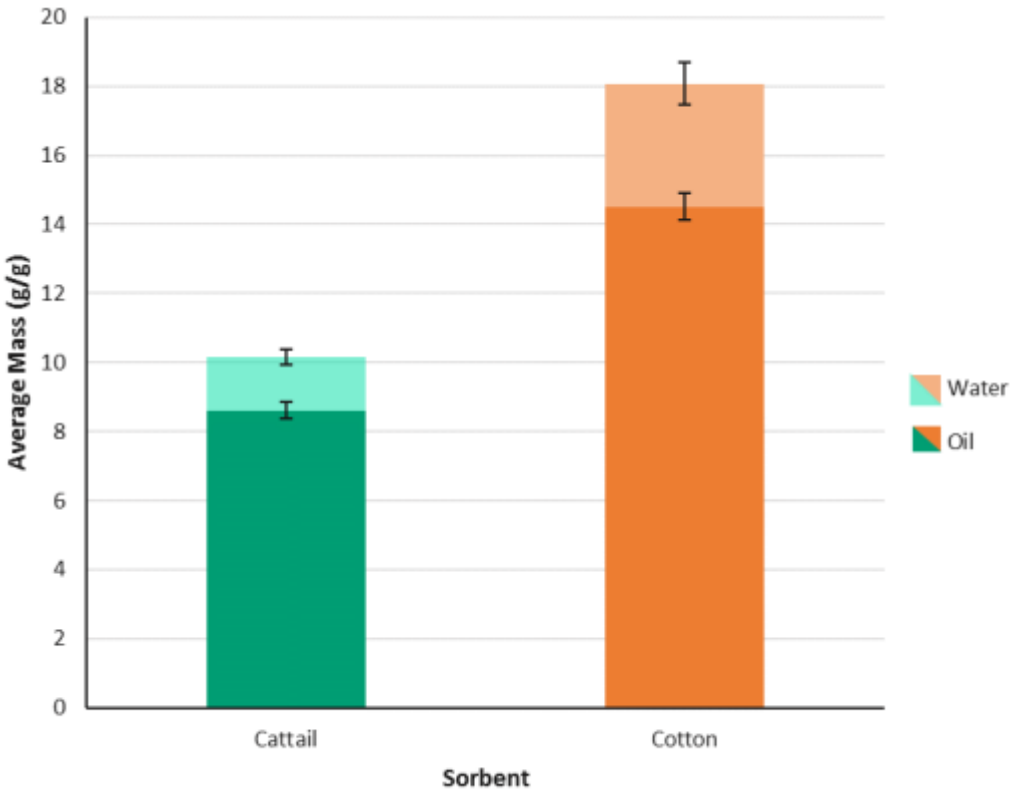

Figure 2.5. Comparison of the average mass (g) of oil and water sorbed by cattail and cotton in an Emulsified Mixture at 25°C

Discussion

Saturation

These results demonstrated that cotton was the most effective material for oil sorption followed by cattail and then rice hulls. Our results showed that sorption was not different between 5-60 minutes of immersion. This makes it difficult to determine the initial rate of saturation, but it was assumed to be less than 5 minutes after which time all materials were saturated. Therefore, we determined that a soaking time of 5 minutes was adequate for full saturation of the sample. This is inconsistent with one literature value that used 15 minutes, but the paper provided no reasoning or explanation as to how that was determined as an

optimal time (Cao et al., 2017). However, another study on kapok fibers also found absorption saturated at approximately 15 minutes (Dong et al., 2015a). To best utilize our lab time, we decided to expose our samples for 5 minutes in solution for future experiments because our results indicated that the fibers reached the same level of saturation as if we had exposed the samples for longer.

At this point, rice hulls were considered ineffective at sorbing oil compared to cattail or cotton. In addition to the very low comparative sorption values, we observed that individual pieces of the hulls would pass through the tulle material while the sample was dripping off the excess oil. This, combined with its poor oil sorption, $1/6^{th}$ that of cattail fiber, led to our discontinuing rice hull study. Razavi (2014) also found very low sorbance in rice hulls at 1.25 g engine oil g^{-1} rice hull.

Drip Time

Based on the findings from the empty, cotton-filled, and cattail-filled packet tests, we concluded that drip times greater than 15 minutes had no significant effect on the calculation of oil retention. A study by Dong *et al.* used a 15 minute drip time with other materials and noted there was no obvious difference in the weight after a longer period of time (2015b). From this analysis, we confirmed that 15 minutes was a valid time interval and to best utilize our lab time, we selected 15 minutes as the lowest acceptable drip time for future methodology.

Sorption of oil was greatest in cotton compared to cattail in all of our trials. This finding was further supported by previous studies comparing different sorbents where they obtained oil sorption capacities of 12 g oil/g cattail and 14.98 g oil/g cotton (Cao et al., 2017). We obtained a larger difference in the oil retained between cattail and cotton, but

these data still demonstrated that cotton had a larger oil sorption capacity relative to that of cattail. It is also of note that the high variability between studies remains unexplained.

Selectivity

We found a 5.6:1 oil to water sorption ratio for cattail fibers and a ratio of 4.0:1 for cotton. Cotton sorbed a greater amount of water than cattail fibers, which was expected. Cotton is less hydrophobic than cattail fibers, due to a lower wax content of 0.6-0.8% compared to that of cattail fibers at 10.64% (Dong et al., 2015b). This property may have allowed cattails to sorb a higher ratio of oil to water as compared to cotton.

Previous studies have implemented several different methods when identifying selectivity. Such is the case in Dong et al., where they exposed their sample to a separated solution of a 1:4 ratio of oil-to-water mixture (2015b). Their selectivity experiment used cattail fibers and cotton in their synthetic assemblies, and achieved oil: water ratios of 88.42:1 and 18.61:1 respectively for assemblies of 90:10 fiber: composite fibers (Dong et al., 2015b). They suggested that cattail fibers possessed higher oil selectivity compared to that of cotton, which agreed with our findings.

Conclusion

Within this phase, we were able to establish a working method to evaluate the sorption of oil and water in two natural product materials, cattail and cotton. We also eliminated rice hulls as an experimental subject due to the combination of poor in oil absorbance and difficulty in making precise measurements. Additionally, the optimal saturation and retention times were established as 5 minutes and 15 minutes respectively. These times were continued throughout our methodology in Phase 2. Both cotton and cattail

fibers were effective in oil sorption but varied in their selectivity for oil vs water. The impact of different water salinity and temperatures on the sorption properties of these materials will be evaluated in Phase 2 of this study.

Chapter III. Phase 2: Temperature and Salinity

Introduction

We have shown previously that cotton fiber sorbs more oil and water than cattail fiber. However, cattail exhibits more selectivity for oil than cotton when placed in a mixture of the two. Phase 2 of our experiment tested the impact of different environmental conditions on sorption by cattail and cotton fibers.

Both temperature and salinity levels have been shown to affect water sorption in natural materials, so we have reason to believe that these factors could affect the selectivity of these two sorbents. There is a diverse range of environments in which oil spills occur due to the global extent over which oil is transported by water. Different bodies of water can be generally classified by their temperature and salinity level, so testing cattail and cotton fibers under these varied conditions is representative of sorbent performance in different waters around the world. To determine how sorption was altered by water temperature or salinity level we measured sorption of cattail and cotton fibers in oil, water, and oil-water mixture. This phase simulates the range of ecosystems in which oil spills occur, allowing us to predict the performance of cattail and cotton fibers in a variety of real-world scenarios.

Methods

Temperature

For the temperature trials, beakers containing 100 mL of SAE 10W-30 motor oil (Castrol Limited, Swindon, England), 100 mL of deionized water or an emulsified mixture of 150 mL oil and 50 mL water were placed in a water bath that was either heated or cooled to 2 ± 1.9°C or 49 ± 1.6°C. Trials at 25 C ± 3.6°C were measured at room temperature without a water bath so were slightly more variable than when the water bath was used to control temperature. Emulsified trials were additionally tested at temperatures of 12 ± 0.7°C and 35 ± 0.5°C. Temperature was controlled with either an ice bath, a Fisher Scientific Isotemp Hotplate (Fisher Scientific, Dubuque, IA), or a B. Braun Thermomix 1480 water bath (B. Braun, Bethlehem, PA). Emulsified solutions were prepared as in Phase 1, Selectivity trials. Eight packets each of cattail or cotton fibers were prepared according to the procedures outlined in Phase 1 and placed in beakers of the appropriate solution for 5 minutes. Packets were then removed and dripped on a drying rack for 15 minutes before being weighed for sorption. Following the initial determination of mass, emulsified packets were placed in a drying oven at a minimum of 50°C and dried until all water was evaporated, as in Phase 1. At this point the packets were reweighed and water sorption was determined as initial mass - final mass after water removal and oil mass was defined at the final mass as in Phase 1.

Salinity

Saline solutions were prepared at concentrations of 0.0301 ± 0.0001 g/mL for ocean-level salinity, 0.0150 ± 0.0001 g/mL for brackish-level salinity, and deionized water with no added salt as the fresh water level (control) using Crystal Sea Marinemix Bioassay Laboratory Formula salt for Marine Environments (Marine Enterprises International,

Baltimore, MD). As in the previous studies for temperature, eight packets each of cattail or cotton fiber were placed in 100 mL solutions of the three salinity levels described as ocean, brackish or freshwater salinity levels. Packets were immersed in these solutions for 5 minutes, removed and dripped for 15 minutes. After this, mass of sorption was obtained as above using the equation final mass - initial packet mass. Water content was calculated as above by oven drying to remove water from the mixtures.

Statistical Analysis

Data were analyzed on Minitab software using ANOVA and the Tukey test, and paired t-tests and two-sample t-tests with a confidence interval of 95% were added as needed. In addition, all graphs were generated using Minitab.

Results

Temperature

Oil sorption

Two-way ANOVA showed a significant effect of both species and temperature on oil sorption at $P < 0.0001$. There was no significant interaction of species by temperature ($P = 0.08$). Oil sorption was greater in cotton compared to cattail (see also chapter 2).

Sorption of oil was reduced in cattail at 12 and 35 C compared to the other temperatures but the pattern of temperature responses was unclear even though the effect of temperature was highly significant (Figure 3.1). Cotton fiber showed decreased sorption at the higher two temperatures, 35 and 49°C (Fig. 3.1)

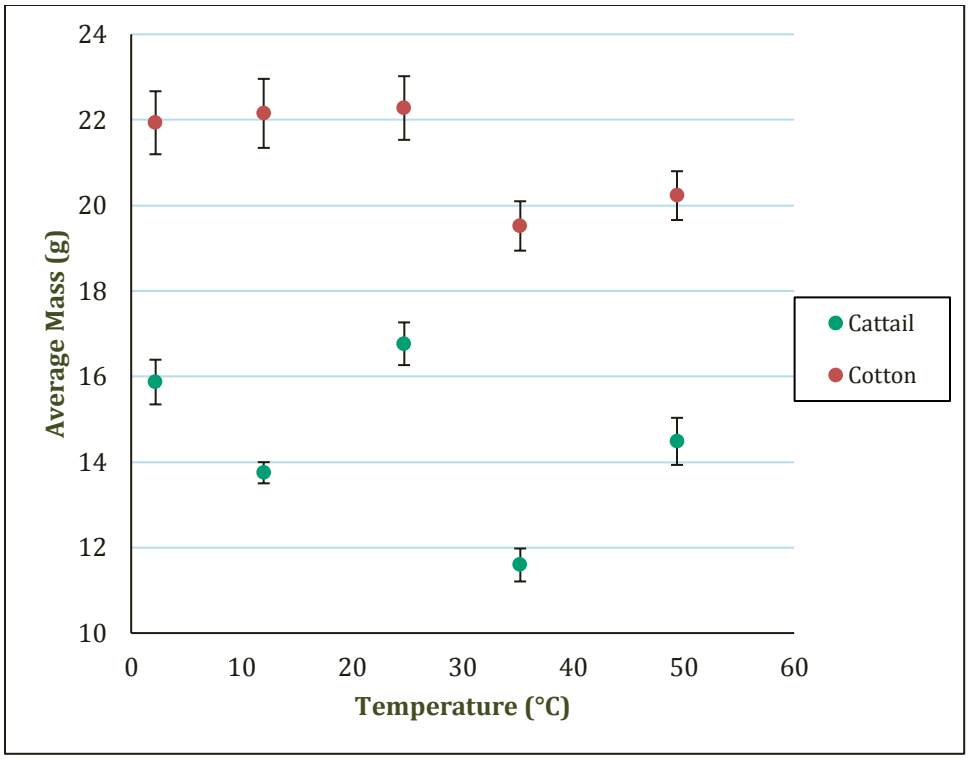

Figure 3.1 Comparison of the average ass (g) of oil sorbed by cattail and cotton at 5 different temperatures. Each value is the mean of 8 samples ± 1 SE and are sorbed mass per 0.50 g of fiber.

Further analysis of the procedures and data suggested that the data were influenced by a systematic error that may have led to differing sorption values in the 12 and 35°C trials. The method of temperature control was different when measurements were made at these two temperatures compared to those made at 2, 25, and 49°C. Also, the 12 and 35C were measured several months apart and it is unclear how storage may have affected sorbance of the fibers. Therefore, for additional analysis we separated the sorption values 12 and 35°C from the values 2, 25, and 49°C for independent analysis. Following this separation of temperature, there was significantly lower sorption at 49°C compared to 25°C (Fig. 3.2A) and 35°C compared to 12°C (Fig. 3.2B). Unfortunately we did not have a common

temperature to normalize these together but for both species, sorption was reduced at the corresponding warmed temperature above 25°C.

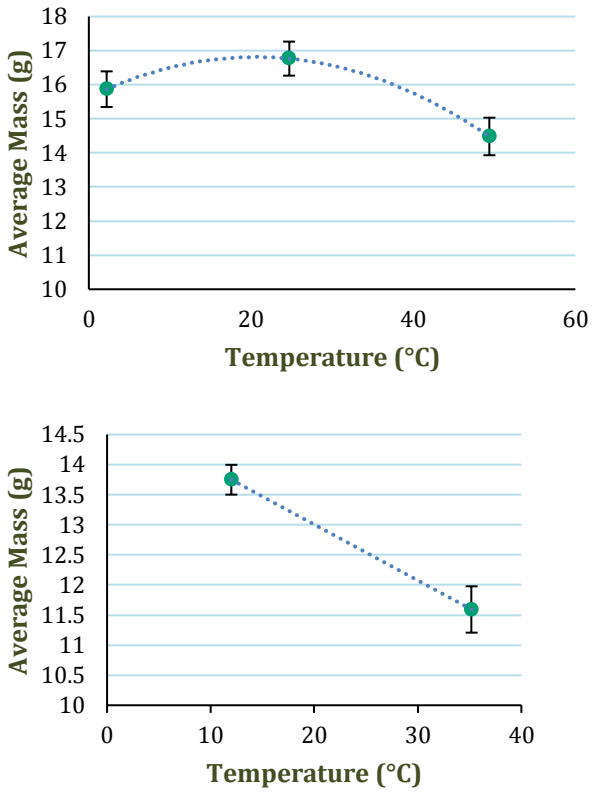

Figure 3.2: Average mass (g) of oil sorbed per 0.50 g of cattail for 2, 25, and 49ºC (left panel) and for 12 and 35.2ºC (right panel)

Water sorption

As in oil there was a significant main effect of fiber type on water sorption ($P < 0.0001$). Temperature was not significant in cattail fiber ($P = 0.133$), but was significant in cotton ($P = 0.014$) (Figure 3.3).

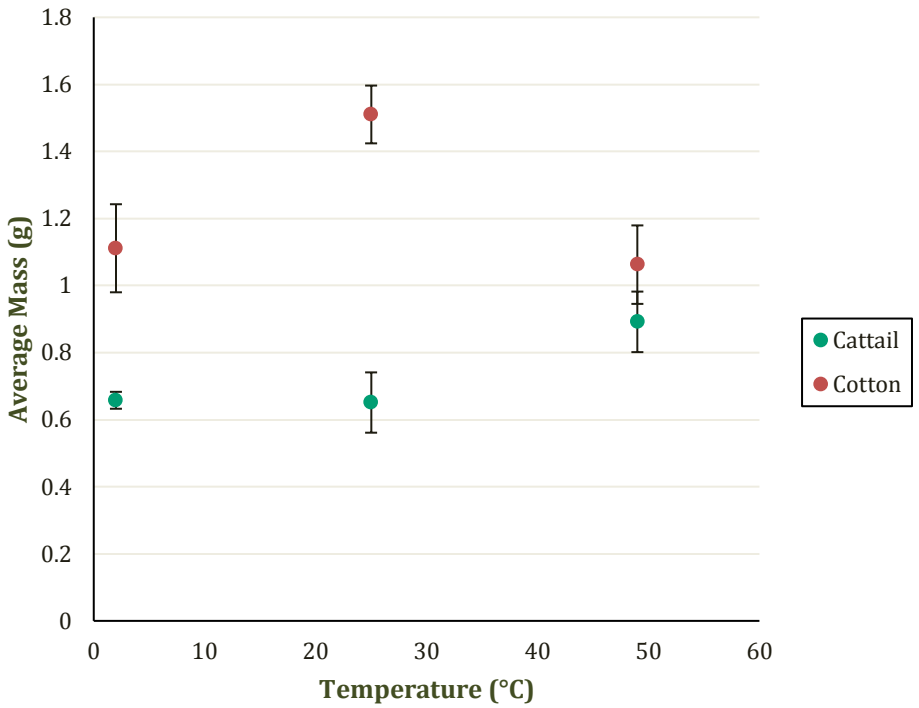

Figure 3.3 Comparison of the average mass (g) of water sorbed per 0.50 g of cattail and cotton at 3 different temperatures. Each point is the mean of 8 replicates ± 1 SE.

Across temperatures, cattail sorbed an average of 1.4672 g water g-1 cattail fiber. Cotton had its highest sorption at 3.0 g water/g cotton fiber at 25°C, about twice that of cattail fiber. Sorption was reduced for cotton at higher and lower temperatures to 1.1 g water/g cotton (Figure 3.3).

Selectivity

Two-way ANOVA showed a significant effect of fiber type on sorption of an emulsified oil-water mixture ($P<0.001$). The average total mass sorbed was 21.6 g mix g^{-1} cattail fiber compared to 35.3 g mix g^{-1} cotton fiber. This does not determine which fiber sorbs more oil when in the presence of oil and water, so further analysis was performed on

the separated values of oil and water (Figure 3.4). Subsequent ANOVA testing showed that temperature was not significant in the total mass sorbed for cotton or cattail fiber, nor did it have an effect on the portions of the total that were comprised of oil or water for either sorbent (Table 3.1).

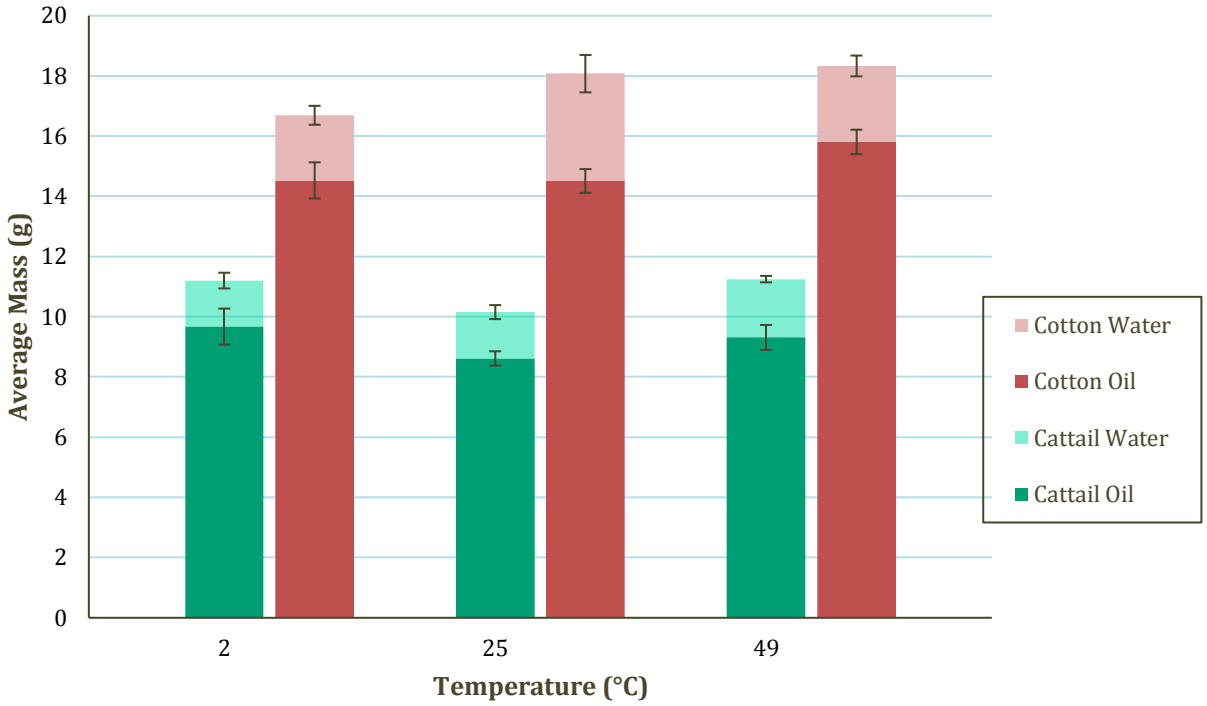

Figure 3.4: Comparison of the average mass (g) of water and oil sorbed per 0.50 g of cattail and cotton in an emulsified mixture at three different temperatures. Each bar is the mean of 8 initial replicates ± 1 SE.

The oil: water ratio of the emulsified solution was 3:1. At 2°C, cattail and cotton fibers performed relatively equally, picking up approximately 6 times as much oil as water encountered with ratios of 6.3:1 and 6.7:1, respectively. At 25°C, cattail fiber (5.6:1) outperformed cotton fiber (4.1:1) while at 49°C, cotton fiber (6.3:1) outperformed cattail fiber (4.8:1).

	P-Value, Cattail Fiber	**P-Value, Cotton Fiber**
Total mass sorbed	0.057	0.087
Oil sorbed	0.286	0.167
Water sorbed	0.515	0.128

Table 3.1: P-values for cattail and cotton fiber in oil-water mixture for temperatures 2.2°C, 24.7°C, and 49.4°C

Salinity

Water sorption

Two-way ANOVA with the Tukey method showed a significant effect of salinity on water sorption in both species and as in previous measurements, cotton generally sorbing a greater mass of water than cattail. However in this case there was a significant interaction with sorbance responding differently to salinity in cotton and cattail fibers. In general salinity increased sorbance in cattail and decreased it in cotton (Figure 3.5).

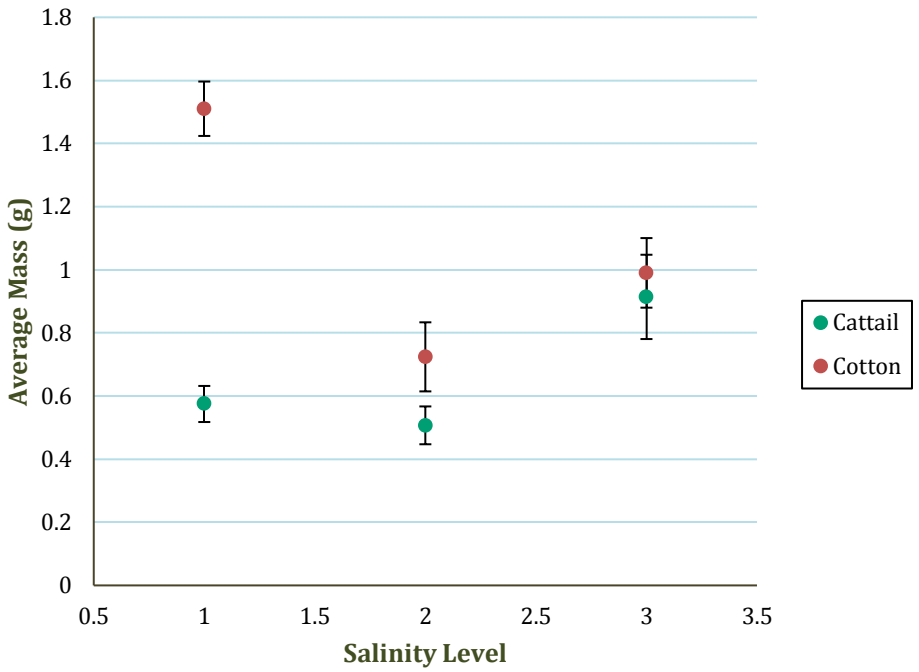

Figure 3.5: Comparison of the average mass (g) of water sorbed per 0.50 g of cattail and cotton at three salinity levels. Each point is the mean of 8 replicates + 1 SE.

For cotton packets, water sorption was significantly ($p < 0.0001$) reduced in bracking and salt water compared to fresh water. Fresh water fibers sorbed 1.51± 0.31g compared to brackish (0.72±0.33 g) or salt water (0.99 ±0.33 g) trials. In cattail, however, sorption was significantly ($P < 0.012$) highest the highest in salt water. In this case salt water trials sorbed 0.91 ±0.404 b of water compared to 0.57 ± 0.20 g in fresh water and 0.51 ±0.19 g in brackish water trials.

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Selectivity

Statistical analysis of ANOVA with a Tukey comparison was run on the data from the oil-water mixes for cotton and cattail packets, which consisted of three sets, 1) total mass of

the oil-water mixture sorbed by the fibers, 2) mass of water sorbed, and 3) mass of oil sorbed (Figure 3.6).

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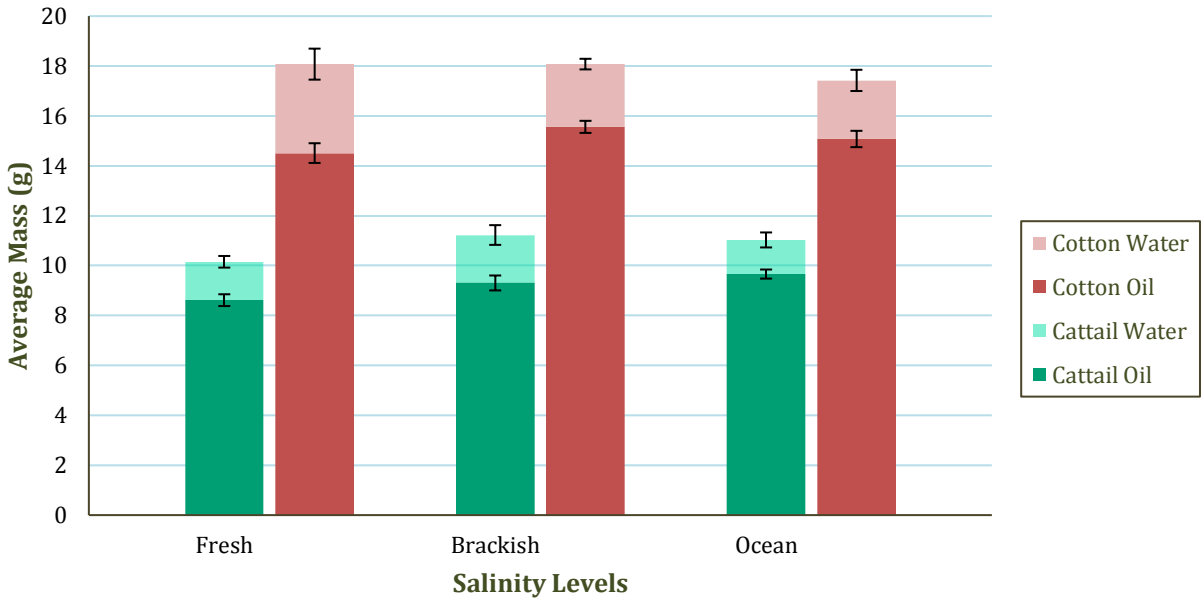

Figure 3.6: Comparison of the average mass (g) of oil (darker shading) and water (lighter shading) sorbed per 0.50 g of cattail (green) or cotton in an emulsified mixture at 25 C. Each bar is the mean of 8 replicates + 1 SE.

Salinity had no effect of total mass, oil or water mass when measured together ($p < 0.834$, $p < 0.284$, $p < 0.123$, respectively). Likewise, in cattail, salinity had as no significant effect on the total mass sorbed or the water sorbed by the cattail packets ($p < 0.127$, $p < 0.507$, respectively). However, oil absorbance significantly increased ($P < 0.030$) in salt water compared to fresh water. Oil sorbed was 9.66 ±0.55 g in salt water and 8.62 ±0.72 g fresh water. for a difference of 1.05 ±0.36 g (95% CI, -1.907, -0.185), $t(7) = -2.87$, $p < 0.024$. Brackish water (9.31 ±0.91 g) trials were not significantly different from either fresh

or ocean water trials. A paired t-test was done on the ocean and fresh water trials to compare this significant difference. Additional paired t-tests were run between the oil sorbed and water sorbed from cotton and cattail packets at each salinity level for materials comparison, similar to the one done for water only trials as described earlier. The oil sorbed at all three salinity levels was different between the two materials ($p < 0.0001$). The water sorbed in the brackish oil-water mix was not statistically different between the two species ($p < 0.137$), but those at the fresh and ocean water trials were significant with a difference of 2.03 ± 82 g (95% CI, 0.-3.964, -0.088), $t(7) = -2.47$, $p < 0.043$, and a difference of 1.30 ±0.35 g (95% CI, -2.130, -0.472), $t(7) = -3.71$, $p < 0.008$.

Selectivity for oil and water was analyzed by comparing the ratios of the oil retained and the water retained at each salinity level and was greatest in cattail in fresh water but this flipped to an advantage for cotton in brackish water and back to cattail in salt water where both oil and water sorption were previously shown to be increased (Table 3.2).

	Fresh	Brackish	Ocean
Cotton	4.0	6.2	5.7
Cattail	5.6	4.8	7.1

Table 3.2 Selectivity (oil to water ratios) values calculated as g of oil sorbed per g water sorbed for cotton and cattail in oil-water mixes at 25 C and at varying salinity concentrations

At the brackish water salinity level, the oil selectivity of cattail fiber decreases to 4.8 compared to 5.6 in fresh water while the cotton oil selectivity increased from 4.0 to 6.2. At

the salt or ocean water salinity level, the oil selectivity of cattail fiber increased to its highest value of 7.1 while the oil selectivity of cotton fiber decreased to 5.7.

Discussion

Temperature

These results confirm that overall, cotton absorbs more oil than cattail as was also shown in Chapter 2 – Phase 1 and previous studies (Cao et al., 2017; Dong et al., 2015 A). However subtle changes in sorption due to temperature, salinity and the selectivity of each material for oil vs water complicate the conclusion that cotton outperforms cattail as a potential natural product for oil spill removal.

The analysis of the temperature response on sorption was complicated because all temperatures were not measured at the same time and we found what appeared to have been a systematic error in the data. Therefore, data were split and analyzed in two groups as shown above. Though the two groups cannot be compared statistically as a single group, it became clear that sorption in both species was reduced at the higher temperature of the grouping and about 25C.

The mechanisms of this reduction are not known but it is possible that this could be due to effects of high oil temperature on the waxes on cation or due to changes in oil viscosity at the higher temperatures. Previous studies have found that oil does not penetrate fibers of the sorbent when it is more viscous as would be the case at the lower temperatures (Teas, 2001). Using the same concept, this also makes the oil much easier to be retained by the sorbent which would explain why less oil was sorbed at higher temperatures. In addition, the 15 minute drip time may not have been sufficient as for the more viscous oil at lower temperatures. Finally, if oil temperature did impact sorption then it may have had a greater

impact on cattail which has more wax than cotton. Dong et al. (2015b) found that cattail fiber has significantly more (10.64%) wax than cotton fiber (0.4-0.8%). At high temperatures, the wax coat could be damaged or destroyed and this wax coating is important in cattail fiber's hydrophobic property. This could be a cause for cattails sorbing more water at higher temperatures. Possibly the wax layer on cotton is thin enough that it does not have a significant impact on hydrophobic properties. Also Dong et al (2015b) did not elucidate the particular wax composition. This information would be important to determine in order to predict the specific impact of temperature on wax content physical properties. More research is needed in this area.

Water sorption was not significantly altered in cattail and this may have also been due to the heavy wax coating of cattail which rendered the fibers virtually hydrophobic at all temperatures tested. However, a small trend of increased water sorption was observed in cattail and this, combined with a significantly reduced oil sorption at high temperatures, could lead to an overall change in efficiency of sorption by cattail fiber in warmer waters.

Sorption of water by cotton was reduced, however at the warmest and coldest water temperature. It is unfortunate that due to time constraints we were not able to measure water sorption at the full suite of temperatures and we therefore cannot rule out systematic error as a possible cause of these results.

The efficiency of any material to be used as a cleanup agent for oil depends on how selective it is for oil. The ideal material would strongly sorb oil and exhibit little sorption for other materials. This would be especially true for water, since our work is particularly focused on oil in waterways as opposed to roadside spills. Removal of oil would become

more physically challenging and expensive as the volume of water unnecessarily removed increased.

As an estimate of this efficiency we tested oil and water sorption in an oil-water slurry and expressed this as the ratio of oil sorbed to that of water sorbed (oil: water). Across all temperatures the average efficiency or oil: water ratio was 6.2:1 in cattail and 5.6:1 in cotton. Therefore, while cotton may sorb more oil, it also sorbs more water and thus overall we predict that it would be a less efficient material for use in oil spills on waterways. The higher water sorbance in cotton could result in a loss of buoyancy in cotton and this would make it an undesirable material for clean-up in waterways if it sank. Further, even if it did not sink, the volume and mass of water collected and transported would be much greater in cotton than in cattail

This generalization however, does have caveats at the warmest temperatures we tested, ca 49°C. At this temperature, the oil: water ratio was reduced to 4.8 in cattail fiber while it was 6.3 in cotton fiber. This is very nearly the exact inverse of the comparison at ca 25°C where the ratio in cattail fiber was at 5.6, compared to only 4.1 in cotton fiber. This suggests that the appropriate material to be used in cleanup operations may change due to water temperature.

Salinity

In the water-only trials, the introduction of salinity (i.e. the distinction between fresh water and higher salinity trials) caused opposite responses in the two materials. We observed a sharp decrease in the amount of water sorbed in cotton and an increase in cattail. The differences were greatly reduced in brackish water and were most apparent only in salt water conditions. When comparing the fibers, the difference between cotton and cattail was nearly

1 gram of water sorbed and was greatest in cotton as in virtually all conditions measured. However, at brackish and salt water conditions the total water absorbance was nearly equal and was not statistically significant. Total water sorbance was greatest in cattail and least in cotton in salt water so in this case the sorbance of the two fiber types converged. This differences could suggest a difference in the mechanism for water sorption between cattail and cotton which could again be related to surface hydrophobicity and/or wax composition or content or simply water potential of the two fibers, which was not measured.

For oil sorbance and across all oil-water mixture trials for cattail fibers, there was a general increase in the amount of oil sorbed parallel to that of water sorbed. Oil sorption by cattail fibers may be more sensitive to salt levels due to a change in the interactions between the oil and water. The primary reason that water salinity is of concern in terms of sorbent effectiveness is because the sorbent will be more buoyant in a higher salinity (and therefore denser) water (Paulauskiene et al., 2014). This means they are less likely to sink as they sorb oil. Because our experiments were conducted in beakers and not in the ocean, the effect of this would be negligible, but could be observed at higher salinity levels or on a larger scale. In this study we used salt concentrations as the lower limits of true salt or ocean water conditions. It is also possible that the increased separation between the oil and water could result from the more buoyant water that forces more oil is on top of the water column. Since the cattails are lighter and more dispersed, they may have higher access to oil rather than cotton which is denser and does not disperse as easily.

Materials comparison with the amount of oil sorbed showed roughly a 5-6 gram difference between cattail and cotton fibers. This reinforces the idea that cattail and cotton fibers continue to show different oil capacities regardless of the salinity level and what we

determined in our initial retention trials from Phase 1. The same materials comparison with the amount of water sorbed showed that water sorption was different with fresh water and ocean water trials, but not brackish water trials, suggesting an altered mechanism of water sorption as aforementioned with the water only trials since a similar trend can be seen where the water absorption for cotton goes down, then up while for cattail goes up, then down. Salinity directly affects water, so water selectivity may be affected by the salt. More research is needed with more salinity levels and higher replication in order to understand how water salinity impacts the potential usefulness of cattail or cotton as a commercial sorbent for oil spill mitigation in open waterways..

Similarly, to temperature selectivity, the average oil to water sorption across all three salinity levels was 5.8:1 for cattails and 5.3 for cotton, which suggests that cattail would be a more selective material to use to pick up oil in waterways, regardless of salinity. There is a general increase in these ratios as salinity increases; however, it is also important to note that at the ocean salinity level, cotton had the same selectivity as cattail had at fresh water salinity. Cattail had the highest ratio of 7.1 at ocean salinity, but is outperformed by cotton at brackish water levels with a ratio of 6.2, further supporting that materials used for cleanup could change depending on the salinity of the contaminated body of water.

By introducing oil into the experiments, the amount of water sorbed by both sorbents increased, which matches the trend for the initial selectivity experiments described in Phase 1 and the temperature selectivity experiments described earlier in Phase 2. This is most likely due to the formation of emulsions. These emulsions were likely formed while homogenizing the mixture of oil and water to get a uniform distribution. Emulsions are water bubbles that are surrounded by oil molecules. If there is a large amount of oil sorption, it is likely that

water was sorbed with the oil through the emulsions. This can explain the increase in water sorption in the mixture trials as opposed to in water-only trials, where it seems unlikely that water would exceed the material's ability to sorb water, but this interaction supports this idea.

There is very limited information available in the literature about the effect of salinity on oil-water selectivity aside from the idea that an increase in salt would cause other materials or less dense liquids to float easily. By attempting to fit our experiments within realistic environmental conditions, it is also important to consider that salinity may have a negligible effect in oil and water sorption in real world cleanup.

Chapter IV. Conclusions and Future Directions

Conclusions

Both cotton and cattail reached saturation capacity within 5 minutes. In previous papers that conducted similar experiments, 15 minutes was used as a drip time, but reasoning behind it was not provided (Dong et al., 2015b).

In our tests for drip time, we observed no significant difference in oil retained between 15 minutes and 4 hours. Because of this we decided to use 15 minutes as the drip time for the rest of our trials which is consistent with previous papers (Dong et al. 2015b). In our selectivity tests, our data support cattail fiber being more selective than cotton fiber. At

room temperature, cattail fiber sorbed 5.6g of oil for every gram of water sorbed while cotton adsorbed 4.0g of oil for every gram of water sorbed.

In the temperature trials, cattail fibers sorbed the most oil at 25°C compared to 49°C, and sorbed more oil at 12.0°C than at 35°C. Cotton was also most effective in oil when sorption occurred at 25 °C. Sorption decreased in both materials when saturation occurred at temperatures greater than 25 °C. This could have been due to the decreased viscosity of the oil at higher temperatures. Oil is more viscous at lower temperatures which makes it more difficult to penetrate the fibers during the absorption process, but also makes it easier to be adsorbed to the fiber's surface (Teas, 2001). This behavior could also be due to the higher temperatures breaking down the fibers wax content. Both sorbents have some wax content which helps them repel water so it is possible it helps sorb oil (Dong et al., 2015b). It is also not known whether the contact with the warm oil would change the water absorption coefficient but other natural materials have been shown to change absorption properties under different temperatures (Mukhopadhyaya et al., 2002). Although differences could be due to wax quantity they could also be due to differences in wax chemical composition or ultrastructure which are not known at this point. Further investigations into wax composition and physical layering and ultrastructure could potentially lead to more detailed hypothesis in this area.

For the water temperature trials, there was no observed effect for the water sorption of cattail fibers which is what was expected. For cotton fibers, water sorption was significantly higher at 25°C than at cooler or warmer temperatures and this also where the selectivity was lowest for cotton. No previous literature could be found to provide an explanation for this. It could be due to an experimental or lab variable that was unaccounted

for. At 2°C and 25°C, cotton sorbed statistically more water than cattail fibers and the sorbents were statistically equivalent at 49°C according to the Tukey test.

In an oil-water mixture, temperature did not have a significant effect on cattail or cotton fibers. Cotton sorbed more water, oil, and mixture than cattail fibers did and this was consistent virtually in every instance measured. While temperature had no effect on the selectivity of cotton, there was a significant trend in cattail fibers. The selectivity of cattail fibers decreased as the temperature of the mix increased. As seen in the water only and oil only trials, cotton has a higher sorption capacity than cattails which showed in the mixture trials. Despite this, cotton and cattail fibers appear to have similar selectivity when comparing the fraction of oil sorbed for each material. For both cotton and cattail fibers, less oil was sorbed in the mixture trials than the oil only trials, but more water was sorbed in the mixture trials than the water only trials. In an emulsified mix like ours, any oil sorbed will also contain water. With the fibers having a limited sorption capability, the water that is sorbed takes the place of oil that would have been sorbed. This is consistent with previous experiments which found fibers sorb less oil in a mixture than in only oil (Dong et al., 2015b). Another notable observation is that temperature had no effect on how much oil was sorbed by cattail fibers in the mixtures despite temperature affecting the oil only trials. If the temperature effect in oil only trials is due to the viscosity, the mixture with water could have changed the properties so that the change in viscosity was negligible.

Limitations with the Study

The largest limitation of this study was that of low replicate number in light of the high variability observed. These could not be avoided given the time and schedule conflict as well as other minor errors which we were unable to spot until it was too late. When

running temperature trials, time constraints in lab combined with difficulty setting up equipment for a specific temperature caused the investigators to run a set of trials at only one temperature as opposed to running trials in the entire range of temperatures. Because of this, we were unable to minimize operating error in our measurements in different sets of temperatures. Similarly, oil only trials for temperatures of 12.0 and 35.2 °C were conducted later than other temperature trials for cattail samples because of time and schedule conflicts. Thus, these trials needed to be analyzed separately from trials for temperatures of 2.2, 24.7, and 49.4 °C. This may have introduced unwanted systematic errors because the sets of data were taken in different days and analyzed differently. Increased replication in all cases especially some of the more variable responses would have greatly increased the statistical power of the study. Unfortunately we were unable to conduct any more trials.

Future Directions

What would be of considerable significance to add to research in cattail fibers' oil sorption ability is research on the fibers' structure and morphology as they may change based on different environmental factors with which we experimented. Based on our conclusions, it would be worthwhile to investigate the effect of temperature on wax content of cattail fibers. Only then can definite correlation between temperature and oil and water sorption be drawn based on degradation of wax content with increase in temperature. Another vital factor that needs further research is how change in oil viscosity at different temperatures affects the way oil sorbs to cattail fibers. A detailed study of cattail morphology may also help shed light on that. Also of importance is the study of chemical characteristics based on varying salinity levels which may help explain some of the trends we observed. For instance, the difference in concentration of ions present in the solution may affect cotton and cattail fibers differently

based on surface chemistry of the materials. Furthermore, as a crucial step in product development, scalability of cattail fibers as a marketable solution to oil spills should be investigated. Spill site simulation and life-cycle analysis must be carried out to evaluate cattail fiber's performance and economic viability in real conditions.

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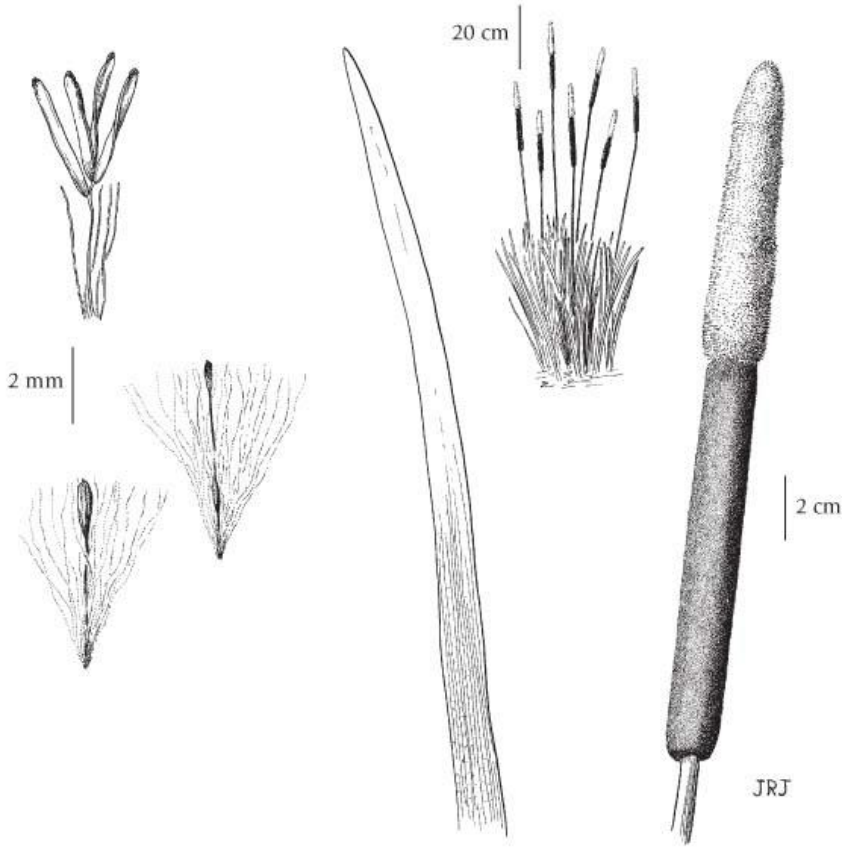
Appendices

Appendix A: Cattail Plant Physiology and Seed Structure



Typha latifolia

Appendix B: Methods Development

Saturation and Retention

Loose cattail fibers, cotton, and rice husks were used in initial retention and saturation experiments. As loose fibers, the sorbent had unrestricted movement, causing a loss in material during the transfer between the scale and the beaker. The saturated samples had to be drained to remove excess oil that had not been adsorbed or absorbed by the sorbent. Draining posed problems for the cattails and rice husk as the mesh used for drainage had gaps that were wide enough for individual pieces of sorbent to slip through into the excess oil beneath. We made attempts to develop a new method to contain the fibers.

Stainless steel ball tea strainers were used as the first attempt. This would allow the oil to reach the sorbent and easier control over the sample; however, material was still lost from placing the fibers into the tea strainers themselves. After the strainers were immersed into the oil, many trials of cattails and cotton showed the oil had not reached the center of the strainer because the fibers were condensed into the small and enclosed space. As a second attempt, we used an impulse sealer and the nylon mesh to contain the sorbent samples. Rice husk was removed as a control as the individual pieces continued to fall through the gaps of the packet and it sorbed a comparatively negligible amount of oil. The sample size was also decreased from 1.0 g to 0.5 g so the oil will be able to reach the center of the packet easily. Due to this change, our samples became enclosed sorbents instead of loose fiber sorbents. This change affects the oil retained in the sorbent because the material's surface area increases. To address this change and possible related errors, we tested for retention, saturation and selectivity in the same manner for all the sorbents from that point forward.

Selectivity

Loose cattail fibers, cotton, and rice husks were used in initial retention and saturation experiments. As loose fibers, the sorbent had unrestricted movement, causing a loss in material during the transfer between the scale and the beaker. The saturated samples had to be drained to remove excess oil that had not been adsorbed or absorbed by the sorbent. Draining posed problems for the cattails and rice husk as the mesh used for drainage had gaps that were wide enough for individual pieces of sorbent to slip through into the excess oil beneath. We made attempts to develop a new method to contain the fibers.

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Temperature

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Appendix C: Growing Cattails

We planned to grow two different species of cattail, narrow leaf (*Typha angustifolia* L) and broadleaf (*Typha latifolia* L.), to use as a source of materials for our study and to compare the sorption properties of the two species. Seeds from hybrid cattail seed heads recovered on campus were planted in the research greenhouse complex in 4 inch diameter pots in the fall of 2014. Potting soil and regular watering was provided by the greenhouse staff. After a month, heat lamps were added to aid in seed germination, which occurred promptly thereafter. Cattail growth was monitored by measuring seedling height from the soil surface. However, we had no method for flooding the seedlings, which prefer to grow in 1 inch of water. As a result, they did not grow successfully in the greenhouse. A second attempt at growing cattails was made by creating a shallow artificial pond. The pond was lined with a waterproof lining and filled with a mixture of half potting soil (Metro Mix PXI), half sand, and a layer of water (maintained at less than 6 inches above the soil surface). 50 narrow leaf and 50 broadleaf 2 inch plugs were planted in two separate artificial ponds in the fall of 2015. Both species continued to grow and thrive throughout our experiments, however, they did not flower their first season (fall 2016) so we were unable to use the seeds from the seed heads to compare sorption properties. We plan to donate both species of cattail to the University of Maryland to be planted around the campus.